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## (54) COMPOSITION CONTAINING INORGANIC LAYERED COMPOUND

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a compsn. which is excellent in dispersion state and stability and gives a film, etc., excellent in gas barrier properties by treating a saponified ethylene-vinyl ester copolymer, an inorg. layered compd., and a solvent contg. a specified amt. of water with a high-pressure dispersion apparatus.

SOLUTION: A saponified ethylene-vinyl ester copolymer, an inorg. layered compd. pref. having an aspect ratio of 50-5,000 and/or a particle size of 1  $\mu$ m or lower (e.g. montmorillonite), and a solvent contg. at least 10 wt.% water (pref. a mixture of water and an alcohol) is subjected to dispersion treatment, pref. under a pressure of 100 kgf/cm<sup>2</sup> or higher, with a high-pressure dispersion apparatus. Pref., the compounding ratio (by vol.) of the inorg. layered compd. to the saponified ethylene-vinyl ester copolymer is (10/1)-(1/100). The compsn. is applied to a substrate and dried to give a laminate excellent in barrier properties against O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub>, water, low-molecular perfume components, etc.

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## CLAIMS

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[Claim(s)]

[Claim 1]An inorganic laminar compound containing composition obtaining by processing a solvent containing 1/10 or more water with a high pressure dispersion apparatus by saponification ethylene-vinyl ester copolymer, inorganic laminar compound, and a weight ratio.

[Claim 2]The inorganic laminar compound containing composition according to claim 1, wherein compounding ratios of an inorganic laminar compound and a saponification ethylene-vinyl ester copolymer are 10 / 1 - 1/100 in a volume ratio (an inorganic laminar compound / saponification ethylene-vinyl ester copolymer).

[Claim 3]The inorganic laminar compound containing composition according to claim 1 or 2 whose aspect ratio of an inorganic laminar compound is 5000 or less [ 50 or more ].

[Claim 4]An inorganic laminar compound containing composition of claim 1-3, wherein particle diameter of an inorganic laminar compound is 1 micrometer or less given in any 1 paragraph.

[Claim 5]An inorganic laminar compound containing composition of claim 1-4 being that in which a high pressure dispersion apparatus carries out distributed processing on pressure conditions more than 100 kgf/cm<sup>2</sup> given in any 1 paragraph.

[Claim 6]An inorganic laminar compound content resin composition obtaining by removing a solvent after processing a solvent which contains 1/10 or more water by saponification ethylene-vinyl ester copolymer, inorganic laminar compound, and a weight ratio with a high pressure dispersion apparatus.

[Claim 7]A constituent containing an inorganic laminar compound containing composition of claim 1-5 given in any 1 paragraph, and other resin.

[Claim 8]A resin composition containing the inorganic laminar compound content resin composition according to claim 6 and other resin.

[Claim 9]23 \*\* per micrometer in thickness of a film produced by removing a solvent, claim 1 characterized by oxygen transmittance in RH (relative humidity) being below 30 cc/m<sup>2</sup> and day-atm 95% - an inorganic laminar compound containing composition given in 5 any 1 paragraphs.

[Claim 10]23 \*\* per micrometer in thickness of a film obtained, the inorganic laminar compound content resin composition according to claim 6 characterized by oxygen transmittance in RH (relative humidity) being below 30 cc/m<sup>2</sup> and day-atm 95%.

[Claim 11]A layered product produced by carrying out spreading desiccation of the inorganic laminar

compound containing composition of claim 1-5 given in any 1 paragraph at a substrate.

[Claim 12]A layered product which has at least one layer of layers which consist of the inorganic laminar compound content resin composition according to claim 6.

[Claim 13]A layered product produced by carrying out spreading desiccation of the constituent according to claim 7 at a substrate.

[Claim 14]A layered product which has at least one layer of layers which consist of the resin composition according to claim 8.

[Claim 15]Mold goods which consist of the inorganic laminar compound content resin composition according to claim 6.

[Claim 16]The mold goods according to claim 15 whose mold goods are films.

[Claim 17]Claim 11 used for packaging applications - a layered product given in 14 any 1 paragraphs.

[Claim 18]The mold goods according to claim 15 or 16 used for packaging applications.

[Claim 19]Claim 11 used for a liquid crystal display - a layered product given in 14 any 1 paragraphs.

[Claim 20]The mold goods according to claim 15 or 16 used for a liquid crystal display.

[Claim 21]Claim 11 used for a protected horticulture use - a layered product given in 14 any 1 paragraphs.

[Claim 22]The mold goods according to claim 15 or 16 used for a protected horticulture use.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to an inorganic laminar compound containing composition.

[0002]

[Description of the Prior Art]In resin, since a saponification ethylene-vinyl ester copolymer (the following EVOH may be called) has high GASUBARIA nature, it has been conventionally used for the wrapping use etc. The constituent which compounded EVOH and an inorganic substance granular material is reported, for example to JP,6-57066,A, JP,1-308627,A, JP,5-39392,A, etc. in order to raise GASUBARIA nature furthermore.

[0003]

[Problem(s) to be Solved by the Invention]However, the constituent which compounded EVOH produced by kneading with a mixer, an extrusion machine, etc. in the Prior art, and an inorganic substance granular material, gas-barrier \*\* of the constituent obtained since distribution of the inorganic substance granular material to the inside of EVOH is not enough -- it was not enough, and in order to improve GASUBARIA nature, when the mixing ratio of the inorganic substance granular material was enlarged, there was a problem that the melt viscosity in the case of kneading increased. the constituents with the good dispersibility of an inorganic substance granular material are gas-barrier \*\*\*\*, such as a film obtained by the ability not to say, also by the method of mixing an EVOH solution and the water dispersion of an inorganic substance granular material, and the method of feeding an inorganic substance granular material into an EVOH solution, and mixing -- it was not satisfactory.

[0004]This invention solves an aforementioned problem and it aims at providing EVOH excellent in the stability which maintains a good dispersion state, and the constituent containing an inorganic laminar compound.

[0005]

[Means for Solving the Problem]This invention persons resulted in this invention, as a result of inquiring wholeheartedly, in order to solve an aforementioned problem. That is, this invention is providing an inorganic laminar compound containing composition obtaining by processing a solvent containing 1/10 or more water with a high pressure dispersion apparatus by saponification ethylene-vinyl ester copolymer, inorganic laminar compound, and a weight ratio.

[0006]

[Embodiment of the Invention] Hereafter, this invention is explained in detail. The saponification ethylene-vinyl ester copolymer used in this invention saponifies an ethylene-vinyl ester copolymer, and can illustrate vinyl acetate, trifluorovinyl acetate, etc. as vinyl ester. From a viewpoint of the GASUBARIA nature of the resin composition obtained, the number of ethylene units to the total-monomers number of unit is percentage, and is 25 to 40% more preferably 20 to 45% 20 to 60%. The degree of saponification of a vinyl ester unit is not less than 98% more preferably not less than 95% not less than 90%. Here, the degree of saponification of a vinyl ester unit means the percentage of the number of saponification vinyl ester units to a number of a vinyl ester unit and a saponification vinyl ester unit of sum totals which exist in EVOH. Commercial trade name Eval (Kuraray Co., Ltd.), trade name SOANORU (Japanese Synthetic chemistry), etc. are more specifically mentioned.

[0007] In this invention, can also use as EVOH what is called an EVOH derivative that has functional groups other than a hydroxyl group, and as functional groups other than a hydroxyl group for example, An amino group, a thiol group, a carboxyl group, a sulfone group, a phosphate group, a carboxylate group, A sulfonic acid ion group, a phosphate anion group, ammonium, phosphonium group, a silyl group, a siloxane group, an alkyl group, an allyl group, a fluoro alkyl group, an ARUKOSHIKI group, a carbonyl group, a halogen group, etc. can be illustrated. Some or all of the hydroxyl group in EVOH may be replaced with one sort of these functional groups, or two sorts or more.

[0008] With the inorganic laminar compound used in this invention. It is the compound thru/or substance in which a unit crystal layer is mutually piled up and has the layer structure, and the layer structure means here the structure in which the field which the atom combined strongly and arranged densely by the covalent bond etc. was piled up almost in parallel with weak coupling power, such as van der Waals force.

[0009] As an example of an inorganic laminar compound, graphite, phosphate system derivation form compounds (phosphoric acid zirconium system compound etc.), a chalcogen ghost, a hydrotalcite compound, lithium aluminum compound hydroxide, a clay system mineral, etc. can be mentioned. A "chalcogen ghost" is dichalcogenate of group IV (Ti, Zr, Hf), V fellows (V, Nb, Ta), and/or a VI group (Mo, W) element, and means here what is expressed with formula  $MX_2$  (M shows the above-mentioned element and X shows chalcogen (S, Se, Te).). The inorganic laminar compound which has swelling and the character which carries out a cleavage from a viewpoint of dispersibility in a solvent which is mentioned later is preferred, and especially the argillite that has swelling and cleavage in a solvent is preferred.

[0010] The following "swelling and cleavage" examinations can estimate the grade of the "swelling and cleavage" nature to the solvent of an inorganic laminar compound. As for the swelling nature of this inorganic laminar compound, in the following swelling examination, it is preferred that it is a grade of about five or more (further about 20 or more). On the other hand, as for the cleavage of this inorganic laminar compound, in the following cleavage examination, it is preferred that it is a grade of about five or more (further about 20 or more). As a solvent, the solvent which has density smaller than the density of an inorganic laminar compound is used in these cases. When an inorganic laminar compound is a natural expansive clay mineral, as this solvent, it is preferred to use water.

[0011] The <swelling examination> inorganic laminar compound 2g is slowly added to solvent 100mL (let a 100mL measuring cylinder be a container). The former (inorganic laminar compound dispersion layer) volume is read from the graduation of the interface of the inorganic laminar compound dispersion layer

after settlement and 23 \*\* and 24hr, and a supernatant fluid. Swelling nature is so high that this figure is large.

[0012]The <cleavage examination> inorganic laminar compound 30g is slowly added to solvent 1500mL, Dispersion machine (the ASADA IRON WORKS CO., LTD. make, Despa MH-L, the diameter of a shuttlecock of 52 mm, and the number of rotations of 3100 rpm) After the peripheral speed of 8.5 m/sec distributes for 90 minutes in the distance of 28 mm between the container capacity 3L and a bottom-shuttlecock (23 \*\*), dispersion-liquid 100mL is taken, it puts into a measuring cylinder, and the volume of an inorganic laminar compound dispersion layer is read from an interface with a supernatant fluid after 60-minute settlement.

[0013]The tetrahedral layer of the type which has the two-layer structure of generally having the octahedral layer which used aluminum, magnesium, etc. as the central metal in the upper part of the tetrahedral layer of silica, and; silica a clay system mineral, It is classified into the type which has a three-tiered structure which consists of both sides the octahedral layer which used aluminum, magnesium, etc. as the central metal by \*\*\*\*. As a former two-layer structure type, kaolinite fellows, antigorite fellows, etc. can be mentioned and a smectite group, a vermiculite group, car owners, etc. can be mentioned with the number of the cations between layers as a latter three-tiered structure type.

[0014]As these clay system minerals, more specifically, Kaolinite, dickite, nacrite, halloysite, antigorite, Chrysotile, pyrophyllite, montmorillonite, hectorite, tetra cyrillic mica, a sodium TENIO light, white mica, margarite, talc, a vermiculite, phlogopite, xanthophyllite, chlorite, etc. can be mentioned. Articles, such as Asakura Publishing Co., Ltd., can be referred to in Haruo Shiramizu work, "argillite study", and 1988.

[0015]By a weight ratio, the solvent used in this invention contains water 1/10 or more, and it as solvents other than water, For example, methanol, ethanol, 2-propanol, 1-butanol, Ether, such as ester species, such as ketone, such as alcohols, such as pentanol, octanol, 1, and 3-pentenediol, acetone, and methyl ethyl ketone, methyl acetate, and ethyl acetate, n-butyl cellosolve, and ethylene glycol, can be illustrated. At least one sort, these solvents may mix two or more sorts, and may be used. It becomes easy to start precipitate etc. rather than the stability of the inorganic laminar compound in the inside of the inorganic laminar compound containing composition in which the content of water is obtained by a weight ratio less than 1/10 is enough.

[0016]From a soluble viewpoint of EVOH, the mixed solvent of water and alcohol is used preferably and methanol, ethanol, 2-propanol, 1-propanol, 1-butanol, etc. can be illustrated as desirable alcohol. In the case of water/alcohol mixed solvent, the compounding ratios of water/alcohol are usually 1 / 10 - 10/1, and are 2 / 8 - 8/2 preferably. The number of alcohol may be one and it may be used two or more kinds.

[0017]When the inorganic laminar compound containing composition which consists of EVOH, inorganic laminar compound, and solvent which are obtained is used as coating fluid etc., As this solvent, it is a fluid near a room temperature, and what transpires easily when drying this constituent is used preferably, and that whose boiling point is 200 \*\* or less (140 more \*\* or less) as this solvent is preferred.

[0018]When mixing EVOH and an inorganic laminar compound, it is preferred to add an inorganic laminar compound in an EVOH solution, heating and agitating is still more preferred on dispersibility, and what has the boiling point of a solvent in not less than (not less than 80 more \*\*) 50 \*\* is preferred. Especially as a solvent from a viewpoint of this boiling point and melting point, water, methanol, ethanol, 1-butanol, 2-propanol, 1-propanol, etc. are preferred. The EVOH dispersion liquid of an emulsion state, etc. may be

used as EVOH, and water / alcoholic mixture dispersion intermediation of carrier fluid of EVOH dispersion liquid is preferred.

[0019]The inorganic laminar compound containing composition of this invention can obtain the constituent outstanding by the dispersibility of the inorganic laminar compound by processing the solvent which contains EVOH, an inorganic laminar compound, and water 1/10 at least by a weight ratio with a high pressure dispersion apparatus. When processing with a high pressure dispersion apparatus, after [ which processed EVOH and an inorganic laminar compound independently ] carrying out post mixing and mixing both beforehand, it may process, but either one of [ at least ] EVOH and an inorganic laminar compound is processed with the solvent containing 1/10 or more water. For example, the dispersion liquid containing an EVOH solution and an inorganic laminar compound are independently processed with a high pressure dispersion apparatus, After processing the dispersion liquid containing the method of processing after mixing the method of mixing later, EVOH, an inorganic laminar compound, and a solvent, and an inorganic laminar compound, with a high pressure dispersion apparatus and mixing EVOH to it, there are a method of processing with a high pressure dispersion apparatus again, etc., but. It is more desirable for the solvent after mixing to contain water 1/10 or more from a viewpoint of the stability of an inorganic laminar compound, when mixing both after processing EVOH and an inorganic laminar compound independently with a high pressure dispersion apparatus.

[0020]Before and after processing with a high pressure dispersion apparatus, a certain operation may be performed to EVOH, inorganic laminar compounds, or those constituents. Mixing, separation, stirring, the dissolution, distribution, heating, cooling, desiccation, defoaming, extraction, settlement, etc. are mentioned to operation. For example, the thing which dissolved EVOH in the solvent, distributed the inorganic laminar compound in water, and mixed them, The constituent produced by adding and stirring additive agents, such as a surface-active agent, to the liquid composition obtained by processing with a high pressure dispersion apparatus and obtaining an inorganic laminar compound containing composition can be conveniently used as coating fluid which is mentioned later.

[0021]When restriction in particular does not have the mixing method, either, when mixing EVOH with an inorganic laminar compound beforehand before processing with a high pressure dispersion apparatus, for example, using an EVOH solution as EVOH, For example, add EVOH first and it is made to dissolve to the water/alcohol mixed solvent which contains \*\*\*\* 1/10 or more, Subsequently, any method may be used although there are two or more methods, such as the method of adding an inorganic laminar compound and distributing, the method of adding also to others in order of an inorganic laminar compound and EVOH, and the method of mixing the dispersion liquid and the EVOH solution of an inorganic laminar compound.

[0022]As for the container used for mixing, what equipped the outer wall with the jacket which can lead heat carriers, such as warm water and steam, for temperature control is preferred. What has a baffle in the inside of a container is used from a viewpoint [ are crowded and ] of a bubble of biting, and achieving equalization of \*\*\*\*\*, and since it is the same, the position of distributed wings is [ to shift a few ] not the center of an iron pot but more preferred (eccentricity). In order for solids concentration to consider it as the comparatively high thing which has good distribution, it is easy to acquire the effect by shearing force with the 4000-7000-rpm high method of carrying out high-speed churning within the iron pot which decompressed the inside to 200 or less mmHg so that a bubble may be blown and it may be hard to be crowded.

[0023]The high pressure dispersion apparatus in this invention is a device which makes the bottom of special conditions, such as high shearing and a high pressure state, by carrying out high-speed passage of the constituent which mixed media which should be distributed, such as particles and a solvent, and making it collide in two or more small tubes. For example, it is preferred that it is preferred to pass the inside of the small tube of 1-1000 micrometers of tube diameters, and the pressure more than 100 kgf/cm<sup>2</sup> requires maximum-pressure conditions for this constituent in a constituent, and more than 500 kgf/cm<sup>2</sup> is more preferred. When a constituent passes through the inside of a high pressure dispersion apparatus, what the highest attainment speed of a constituent reaches [ sec ] in not less than 100 m /is preferred, and the thing of rate of heat transfer of 100 or more kcal/hr is preferred.

[0024]The principle of the high-pressure-treatment part within the high voltage distributed processing device used in this invention in drawing 1 was shown typically. High voltage is applied to a processing sample in the small tube portions of (C) and (D) with the pump of (B) among drawing 1. And when the rate of flow of the point which reaches top speed momentarily is 300 m/sec, for example, it passes through the inside of the cube of volume  $1 \times 10^{-3} \text{ m}^3$  by  $1/(3 \times 10^5) \text{ sec}$  and sample temperature rises by 35 \*\*, energy is transmitted to a sample by pressure loss. Rate of heat transfer serves as  $3.8 \times 10^4 \text{ kcal/hr}$ , when the specific gravity of a sample is  $1 \text{ g/cm}^3$  and specific heat  $1 \text{ cal/g}^{**}$ .

[0025]As this high pressure dispersion apparatus, there is an ultra-high pressure homogenizer by Microfluidics Corporation (trade name Micro fluidizer) or a nano mizer by a nano mizer company, for example, The Menton Gaulin type high pressure dispersion apparatus, for example, the Izumi Food Machinery homogenizer etc., is mentioned to others. When using a Micro fluidizer as a high pressure dispersion apparatus, as for a processed material, it is preferred to have mobility at the temperature which processes, and it is preferred to use the EVOH solution which dissolved EVOH in the solvent.

[0026]When using it, coating the inorganic laminar compound containing composition of this invention, the higher possible one of the viewpoint of desiccation after coating to total-solids concentration is preferred, and it is preferred that EVOH and an inorganic laminar compound are high concentration as much as possible.

[0027]Although the composition ratio (volume ratio) in particular of an inorganic laminar compound and EVOH is not limited, they are usually 10 / 1 - 1/100, from a viewpoint of GASUBARIA nature, as for the volume ratio (ratio in the case of "preparation") of an inorganic laminar compound/EVOH, 5/95 or more is preferred, and 90/10 or less is preferred [ a volume ratio ] from a viewpoint of a moldability. From a viewpoint of the pliability of the mold goods obtained, 5 / 95 - 30/70 have a preferred volume ratio, and especially 10 / 90 - 30/70 are preferred. When using it as a film or a layered product, from a point of control of the physical-properties fall by bending, it is preferred that a volume ratio is 7/93 or more, it is inflexible and it is preferred that it is 17/83 or less from a viewpoint of controlling the exfoliation from a substrate.

[0028]By each density, the above-mentioned volume ratio can carry out division process of the numerator (weight of an inorganic laminar compound) of the weight ratio in the case of "preparation" of these ingredients, and the value of a denominator (weight of EVOH), and can calculate them.

[0029]On a coating disposition, for the purpose, such as viscosity control, various solvents can be blended with the inorganic laminar compound containing composition of this invention, or an additive agent can be blended with it if needed. As an example of an additive agent, paints, a surface-active agent, an antifungal



agent, an antiseptic, a cross linking agent, a defoaming agent, an antioxidant, etc. are mentioned.

[0030]As paints, the rust preventive pigment for primers, a color pigment, metallic foil paints, photoluminescent pigment, an extender, etc. can be illustrated. As a rust preventive pigment for primers, strontium chromate, zinc chromate, zinc phosphate, red lead oxide, a flower of zinc, basic sulfate, basic carbonate, etc. are mentioned. As a color pigment, copper phthalocyanine blue, Phthalocyanine Green, KINAKU drine compounds, indanthrone, isoindolinone, BERIREN, ANSURA pyrimidine, benz imidazolone, carbon black, a titanium dioxide, black lead, Synthetic Ochre, red oxide of iron, etc. are mentioned.

[0031]As metallic foil paints, aluminium foil, bronze foil, tinfoil, gold foil, silver leaf, copper foil, titanium metal foil, stainless steel foils, nickel foil, chromium foil and the alloy foil of the metal mentioned above, the metallic foil covered with the plastic, etc. are mentioned.

[0032]As photoluminescent pigment, mica foil, foil form copper phthalocyanine blue, etc. are mentioned, and calcium carbonate, gypsum fibrosum, clay, talc, etc. are mentioned as an extender.

[0033]As a surface-active agent, it can be used in consideration of workability, such as stability of a treating solution, fizz, and spreading nature, out of arbitrary surface-active agents, such as a non-ion system, a negative ion system, a positive ion system, and a both sexes system, for example, selecting suitably.

[0034]As a non-ion system surface-active agent, polyoxy ethylene glycol, polyoxyethylene polyoxypropylene glycol, Polyoxypropylene glycol, polyoxyethylene alkyl phenyl ether, Glycerin fatty acid part ester, sorbitan fatty acid part ester, pentaerythritol fatty acid part ester, polyoxyethylene sorbitan acid fat partial ester, and polyoxyethylene alkyl ether are mentioned.

[0035]As a negative ion system active agent, dialkyl sulfosuccinate, an alkane-sulfonic-acid salt, Alkylbenzene sulfonates, alkyl naphthalenesulfonate, A polyoxyethylene alkyl sulfophenyl ether salt, an alkyl phosphoric ester salt, A polyoxyethylene-alkyl-ether phosphoric ester salt, the sulfuric ester salt of aliphatic alkylester, alkyl-sulfuric-acid ester salt, polyoxyethylene-alkyl-ether sulfuric ester salt, and fatty acid monoglyceride sulfuric ester salt are mentioned. As a positive ion system active agent, an alkylamine salt and a dialkyl amine salt are mentioned and N,N,N-trialkyl N-sulfo alkylene ammonium betaine is mentioned as a both sexes system.

[0036]As an antifungal agent and an antiseptic, quarternary ammonium salt, a nitrogen-containing sulfur compound, a halogen-containing nitrogen sulfur compound, an organic iodine system compound, a benzimidazole system compound, etc. can be used. As an antifungal agent, specifically 2-thiazoly-4-ylbenzimidazole, Methylbenzimidazole-2-ylcarbamate, N-dichlorofluoro methylthio N',N'-dimethyl- N-phenylsulfamide, Tetramethyl thiuram disulfide, the N-(trichloro methylthio)-4-cyclohexene 1, 2-dicarboxyimide, Although there are 2,4,5,6-tetrachloro-1,3-isophthalonitrile and 2,3,5,6-tetrachloro-4-(methylsulfonyl) pyridine, the bis(2-pyridylthio)-zinc 1, 1-dioxide, etc., If heat resistance is taken into consideration, 2-thiazoly-4-ylbenzimidazole, methylbenzimidazole-2-ylcarbamate and 2,4,5,6-tetrachloro-1,3-isophthalonitrile, the bis(2-pyridylthio)-zinc 1, and 1-dioxide are preferred.

[0037]As a \*\* bacteria agent, 1,2-benzoiso thiazoline 3-one (BIT), 2,3,5,6-tetrachloro-4-(methylsulfonyl) pyridine, a 10,10'-oxyscrew phenoxyarsine, etc. are specifically used.

[0038]As a cross linking agent, a titanium system coupling agent, the Silang system coupling agent, a melamine system coupling agent, an epoxy system coupling agent, an isocyanate system coupling agent, a copper compound, a zirconium compound, etc. are mentioned. From a point of waterproof improvement, a zirconium compound is used especially preferably. As an example of a zirconium compound, for example

Zirconium oxychloride, Zirconium halides, such as a hydroxyzirconium chloride, a zirconium tetrachloride, and zirconium bromide; Zirconium sulfate, Zirconium salt of mineral acid, such as basic zirconium sulfate and a zirconium nitrate; A formic acid zirconium, An acetic acid zirconium, a propionic acid zirconium, a caprylic acid zirconium, Zirconium salt of organic acid, such as a stearic acid zirconium; Zirconium carbonate ammonium, Zirconium complex salt [, such as zirconium sulfate sodium, acetic acid zirconium ammonium, and zirconium sodium oxalate, citrate zirconium sodium, and citrate zirconium ammonium, ]; etc. are raised. Although the addition in particular of a cross linking agent is not limited, it is preferred that the ratio ( $K=CN/HN$ ) of the number of mols of the bridge construction generation group of a cross linking agent (CN) and the number of mols of the hydrogen bond nature group of resin (HN) uses so that it may become or more 0.001 ten or less range. the ratio of this number of mols -- as for K, it is still more preferred that it is or more 0.01 one or less range.

[0039]When using the inorganic laminar compound containing composition of this invention for coating furthermore, a solvent can be added in order to raise the wettability at the time of coating more. What has transpired when the solvent was a fluid near the room temperature, and it applies to a substrate and it is dried alone is used preferably. Alcohols, such as methanol, ethanol, 2-propanol, 1-butanol, a pentanol, and octanol, acetone, methyl ethyl ketone, ethyl acetate, etc. are mentioned to this. Two or more kinds of solvents may be used. Thus, coating is carried out or the prepared liquid can be used with dip coating and the brush, applying.

[0040]The following is mentioned as an index of dispersibility evaluation of the inorganic laminar compound in the inorganic laminar compound containing composition of this invention. How for cast film production etc. to use a constituent as smooth substrates (for example, glass plate etc.) thinly, and judge by the appearance comparison when it is the liquid composition currently distributed by the solvent (if it is a maldistribution) The method of judging by whether the mean particle diameter (R) of which of an inorganic laminar compound when an EVOH solution or dispersion liquid distribute is close to the value of  $R_0$ , etc. are raised on the basis of the mean particle diameter ( $R_0$ ) of an inorganic laminar compound when carrier fluid distributes independently which can carry out the visual judgment of the aggregate.

[0041]The method by the method of diffracting/being scattered about, the method by dynamic light scattering, the method by electrical resistance change, the method by image processing after microscope photography, etc. are possible for the method of asking for the mean particle diameter of the inorganic laminar compound in a constituent. Since there is little dispersion on parenchyma (that is it is transparent), it is not concerned with the existence of resin but the information only on the particle size distribution of an inorganic laminar compound is acquired when dispersion of inorganic laminar compound origin is dominant, the method by the method of diffracting/being scattered about is used for a constituent comparatively preferably.

[0042]The particle size distribution and mean-particle-diameter measurement by the method of diffracting/being scattered about are made by calculating the particle size distribution which does not have inconsistency in a pattern using Mie-scattering theory etc. in the diffraction/scatter pattern obtained when dispersion liquid are made to pass light. As a commercial device, it is coal tar company make. Laser diffraction and light scattering measurement Particle-size-analysis device LS230, LS200, LS100, Shimadzu make Laser diffraction type size distribution measuring device SALD2000, SALD2000A, SALD3000, Horiba laser-diffraction-and-scattering type size distribution measuring device LA910, LA700, LA500, Nikkiso

make The micro track SPA, the micro track FRA, etc. are raised.

[0043]It is preferred to measure without dilution in the case of particle-size-distribution measurement. In the case of liquid with too strong dispersion and a low light transmittance state, liquid can be measured without dilution by taking short light path length (for example, in the case of Horiba LA910, light path length can be remarkably shortened in a batch type cell, a paste cell, etc.). However, when it dilutes with the solvent of liquid solvent composition and the presentation, dispersibility may not change in many cases, and measuring a diluent in that case may estimate dispersibility.

[0044]In this measuring method, since it will become impossible to separate and identify particles if the distance between particles is below the wavelength of a light source, a certain amount of distance (for example, below a submicron) is separated, and two or more close (intervening resin etc. in between) particles are recognized to be one particle. For this reason, this method can also estimate the maldistribution which produces not only the maldistribution by condensation of particles but resin by intervening.

[0045]As an inorganic laminar compound used in this invention, that the viewpoint of GASUBARIA nature to whose aspect ratio is 5000 or less [ 50 or more ] is preferred. An aspect ratio (Z) is a ratio calculated from the relation of  $Z=L/a$  here. It is the particle diameter (median size of a volume reference) of the inorganic laminar compound for which it asked with the particle diameter measuring method by the method of diffracting/being scattered about which L described above among dispersion liquid here, and a is the unit thickness of an inorganic laminar compound. This "unit thickness a" is a value decided by the powder X-ray diffraction method etc. which are mentioned later based on inorganic laminar compound independent measurement. As more specifically typically shown in the graph of drawing 1 which took 2 theta along the horizontal axis and took the intensity of the X diffraction peak along the vertical axis, From the angle theta corresponding to the peak by the side of a low angle, most among the diffraction peaks observed. The interval searched for based on the formula ( $n\lambda=2D\sin\theta$ ,  $n= 1, 2, 3 \dots$ ) of Bragg is set to "unit thickness a" (Jiro Shiokawa editorial-supervision "guidance (a) of instrumental analysis" 69-page (1985) Kagaku-Dojin issue can be referred to for the details of a powder X-ray diffraction method, for example).

[0046]When the powder X-ray diffraction of the resin composition which removes a solvent from dispersion liquid is carried out, it is usually possible to search for the spacing d of the inorganic laminar compound in this resin composition. As more specifically typically shown in the graph of drawing 2 which took 2 theta along the horizontal axis and took the intensity of the X diffraction peak along the vertical axis, Let the interval corresponding to the peak by the side of a low angle be "the spacing d" ( $a<d$ ) most among the diffraction peaks observed at the low angle (interval is large) side from the diffraction peak position corresponding to the above-mentioned "unit thickness a." As typically shown in the graph of drawing 3, in the case where it is difficult for the peak corresponding to the above "spacing d" to lap with halo (or background), and to detect, area of the portion excluding the baseline by the side of a low angle from 2thetad is made into the peak corresponding to "the spacing d." It is an angle of diffraction by which "thetad" corresponds here at "+ (unit length a) (width of a resin single strand)" (Asakura Publishing Co., Ltd. can be referred to for the details of the method of determining this spacing d in the volumes for rock student Shuichi, "a clayey encyclopedia", 35 pages or less and 271 pages or less, and 1985, for example).

[0047]Thus, as for "integrated intensity" of the diffraction peak (it corresponds to the spacing d) observed in the powder X-ray diffraction of a resin composition, it is preferred that it is two (further 10 or more) or more

in the relative ratio to the integrated intensity of the diffraction peak (it corresponds to "the spacing  $a$ ") used as a standard. Usually, the difference of the above-mentioned spacing  $d$  and "unit thickness  $a$ ", i.e., the value of  $k = (d - a)$ , is equal to the width of the resin single strand which constitutes a resin composition (when it converts into "length"), or it is size from this (width of a  $k = (d - a) \geq$  resin single strand). Although such "width of a resin single strand" can be asked by simulation computation etc. (for example, in the case of reference) and polyvinyl alcohol, it will be 4-5 Å about Kagaku-Dojin in a "high-polymer-chemistry introduction", 103-110 pages, and 1981 (a water molecule 2-3 Å).

[0048] There is validity in above-mentioned aspect ratio  $Z = L/a$  having this aspect ratio  $Z$ , and approximating "a true aspect ratio" for the following reason. That is, direct measurement is very difficult for "the true aspect ratio" of the inorganic laminar compound in a resin composition. The relation between "unit thickness  $a$ " called for on the other hand by the spacing  $d$  and the inorganic laminar compound independent powder X-ray diffraction measurement which are called for by the powder X-ray diffraction method of a resin composition which becomes in  $a < d$  is, And when the value of  $(d - a)$  is more than the width of the resin single strand in this constituent, resin will be inserted between the layers of an inorganic laminar compound into the resin composition. Therefore, there is sufficient validity in approximating "the true aspect ratio" under approximating the thickness of the inorganic laminar compound in a resin composition above "unit thickness  $a$ ", i.e., a resin composition, by "aspect ratio  $Z$ " in the inside of the dispersion liquid of the above-mentioned inorganic laminar compound.

[0049] As mentioned above, true particle diameter measurement in a resin composition is very difficult, but it is possible that the particle diameter of the inorganic laminar compound in the inside of resin is quite as near as the particle diameter of the inorganic laminar compound in dispersion liquid (resin / inorganic laminar compound / solvent). However, the particle diameter  $L$  in the inside of the dispersion liquid called for by the method of diffracting/being scattered about. Since it is thought that a possibility of exceeding the major axis  $L_{\max}$  of an inorganic laminar compound is quite low, the true aspect ratio ( $L_{\max}/a$ ) of a possibility of being less than "aspect ratio  $Z$ " used by this invention ( $L_{\max}/a < Z$ ) is quite low theoretically.

[0050] It is thought that the definition  $Z$  of an aspect ratio used by this invention has sufficient validity from two points mentioned above. An "aspect ratio" or "particle diameter" as used herein means "aspect ratio  $Z$ " defined above or the "particle diameter  $L$  for which it asked by the method of diffracting/being scattered about."

[0051] 50 or more have the preferred aspect ratio mentioned above from a viewpoint of GASUBARIA nature, as for the inorganic laminar compound used for this invention, 100 or more are more preferred, 200 or more are still more preferred, and 500 especially or more are preferred. From a viewpoint of manufacturability, as for an aspect ratio, 5000 or less are preferred, 3000 or less are more preferred, 2000 or less are still more preferred, and 1500 especially or less are preferred.

[0052] As for the particle diameter measured by the method which the inorganic laminar compound used for this invention mentioned above, it is preferred that it is 5 micrometers or less from a viewpoint of a moldability, and it is preferred from a viewpoint of transparency that it is 3 micrometers or less. As for this particle diameter, when transparency uses for the use (for example, packaging applications of foodstuffs) thought more as important, it is preferred that it is especially 2 micrometers or less.

[0053] Other resin other than EVOH may be further added to the inorganic laminar compound containing composition of this invention. As other resin, for example, polyethylene (low density, high density), ethylene

propylene rubber, Polyolefin system resin, such as an ethylene-butene copolymer, an ethylene-hexene copolymer, an ethylene-octene copolymer, polypropylene, an ethylene-vinylacetate copolymer, an ethylene-methyl methacrylate copolymer, and ionomer resin, can be illustrated.

[0054]The inorganic laminar compound containing composition of this invention obtained by the above can remove a solvent by desiccation etc., and can use it as an inorganic laminar compound content resin composition. Other resin other than same EVOH may be mixed with having mentioned above to the obtained inorganic laminar compound content resin composition. The mixing method can illustrate the usual method used for mixing of resin.

[0055]The inorganic laminar compound containing composition of this invention can be used as a cast by the cast producing-film method etc. On a substrate which is mentioned later, spreading desiccation can be carried out and it can also be considered as a layered product. As a manufacturing method of a layered product, the method of pasting together to a substrate what dried and film-ized the inorganic laminar compound containing composition (methods, such as cast film production) afterwards, the coating method which carries out spreading desiccation of the constituent at a substrate, etc. are usually used, and especially the latter is used preferably, for example.

[0056]As a coating method, the direct photogravure method, the reverse photogravure method, and the micro photogravure method, Methods, such as a coating method which combined the roll coating methods, such as the 2 roll beat coat method and the bottom product three feeding reverse coat method, and the doctor knife method and the die coat method, a dip coating method, the BAKOTINGU method, and these, are mentioned.

[0057]When considering it as a layered product, although a layered product is based on the target character, as for the thickness of the layer formed from an inorganic laminar compound containing composition, 30 micrometers or less are preferred at dried thickness, and its 10 more micrometers or less are more preferred. Since the transparency of the layer formed from a constituent in 1 micrometer or less also doubles and has the strong point in which it is remarkable and high, for the use of required this invention of transparency, it is still more desirable. Although there is no restriction in particular about a minimum, especially in order to acquire an effect, it is preferred that it is not less than 100 nm not less than 10 more nm 1 nm or more.

[0058]A substrate in particular is not limited but there is no restriction in gestalten, such as film state, a sheet shaped, the shape of a bottle, and the shape of a tray. As the construction material, it is usable according to the purpose and a use in publicly known thru/or general things, such as resin, paper, aluminum foil, wood, cloth, and a nonwoven fabric. When it is especially film state, it may be extended by one axis and biaxial besides not having extended. Of course, a publicly known under coat, corona treatment, etc. may be carried out, and these surface treatments may be made about the substrate of not only film state but the other gestalt in the range which does not lose the purpose of an invention.

[0059]As resin which constitutes a substrate, polyethylene (low density, high density), ethylene propylene rubber, An ethylene-butene copolymer, an ethylene-hexene copolymer, an ethylene-octene copolymer, Polypropylene, an ethylene-vinylacetate copolymer, an ethylene-methyl methacrylate copolymer, Polyolefin system resin, such as ionomer resin; Polyethylene terephthalate (PET), the polyester system resin; nylon 1, such as polybutylene terephthalate and polyethylenenaphthalate, -- 6, nylon 6, 6, and meta xylenediamine adipic acid polycondensation polymer. amide system resin [, such as polymethyl

methacrylic imide, ]; -- acrylic resin [, such as polymethylmethacrylate, ]; -- polystyrene. A styrene acrylonitrile copolymer, a styrene acrylonitrile butadiene copolymer, Styrene thru/or acrylonitrile series resin, such as polyacrylonitrile; Tori cellulose acetate, Hydrophobing cellulose type resin, such as JI cellulose acetate; Halogen-containing-resin; polyvinyl alcohol, such as polyvinyl chloride, a polyvinylidene chloride, polyvinylidene fluoride, and polytetrafluoroethylene (Teflon), an ethylene-vinylalcohol copolymer, Hydrogen bond nature resin, such as a cellulosic; Polycarbonate resin, polysulphone resin, Engineering-plastics system resin, such as polyether sulfone resin, polyether ether ketone resin, polyphenylene oxide resin, polymethylene oxide resin, and liquid crystal resin, etc. are mentioned.

[0060]It can laminate to the substrate which could also use the inorganic laminar compound content resin composition mentioned above as mold goods, such as a film, by the usual method, and was mentioned above by the usual methods, such as coating, pasting, and co-extrusion, and can also be considered as a layered product.

[0061]As for the above-mentioned inorganic laminar compound containing composition and an inorganic laminar compound content resin composition, it is preferred to have transparency, when a substrate is a transparent material. This transparency is total light transmittance with a wavelength of 500 nm, and it is preferred that it is not less than (not less than 85 more% especially not less than 90%) 80% of grade. For example, such transparency can be suitably measured with a commercial spectrophotometer (Hitachi make and recording spectrophotometer 330 type). About the degree (HAZE) of cloudy weather, 25% or less is preferred, especially 15% or less is preferred 20 more% or less, and a commercial hazemeter (made by Suga Test Instruments) is used for measurement.

[0062]The layered product which can obtain the inorganic laminar compound containing composition and inorganic laminar compound content resin composition of this invention by producing a film or laminating is used for various uses. For example, it can use for the protected horticulture use etc. which are used for institutions using the low molecule diffusion lagged effect by the phase difference film and the layer structure using the double reflex, such as a gas, a low molecule diffusion interception nature film and a cast, a house for agriculture, and a tunnel. When using for the packaging applications of foodstuffs and drugs as a gas-barrier-properties film, it can use as a cast by laminating printing and other films further to this film.

[0063]The film produced from a viewpoint of GASUBARIA nature by removing a solvent from the inorganic laminar compound containing composition of this invention, And 23 \*\* with a thickness of 1 micrometer of the film which consists of an inorganic laminar compound content resin composition, It is preferred that the oxygen transmittance under 50%RH is below  $30 \text{ cc/m}^2$  and day-atm, it is below  $5 \text{ cc/m}^2$  and day-atm, things are more preferred, and it is still more preferred that it is below  $1 \text{ cc/m}^2$  and day-atm. When using for the use of which GASUBARIA nature is required more, below  $0.1 \text{ cc/m}^2$  and day-atm are preferred, it is [ below  $0.05 \text{ cc/m}^2$  and day-atm ] still more desirable, and below especially  $0.02 \text{ cc/m}^2$  and day-atm are preferred.

[0064]

[Effect of the Invention]According to this invention, the constituent which consists of EVOH and an inorganic laminar compound and which was distributed good can be obtained, and a film and a sheet excellent in GASUBARIA nature can be obtained by fabricating this constituent. It the layered product is

not only excellent in oxygen interception nature, but is remarkably excellent in interception nature, such as low-molecular aroma components, such as other gas molecules, for example, helium, nitrogen, carbon dioxide, water, limonene, and menthol. \*\*[0065]

[Example] Hereafter, although an example explains this invention in detail, this invention is not limited to these.

[0066][Example 1] It supplied stirring high grade montmorillonite (trade name KUNIPIAK; made by Kunimine Industries) 1 weight section to underwater [ of 100 weight sections ] as an inorganic laminar compound, and the montmorillonite water dispersion of concentration was prepared about 1% of the weight by the method of stirring until it becomes uniform liquid dispersedly. Stirring these dispersion liquid violently, 2-propanol of 350 weight sections and 1-butanol of 25 weight sections were added gradually, and it was considered as the dispersion liquid that the weight ratio of carrier fluid is set to water / 2-propanol / 1-butanol = 2/7.5/0.5. Let this be A liquid.

[0067] EP-F101 (EVOH by Kuraray Co., Ltd., the rate of the formation of ethylene copolymerization; hereafter 32%) It dissolved by supplying five copies described as EVOH-F to 95 copies of solvents mixed by the weight ratio of water/2-propanol = 3/7, heating them at about 80 \*\*, and stirring them for 4 hours, and 5% of the weight of the EVOH-F solution was obtained. Let this be B liquid. Here, 56 copies of A liquid and 694 copies of B liquid were mixed, and 750 copies of C fluid was obtained. The solids concentration which weight ratios are water / 2-propanol / 1-butanol = 21/74/5 in the solvent of water / 2-propanol / 1-butanol, and asked for C fluid from calculation is 0.56 % of the weight.

[0068] Uniform dispersion liquid with good dispersibility was obtained by processing this C fluid once by through and 1750 kgf/cm<sup>2</sup> to a high pressure dispersion apparatus (trade name: ultra-high pressure homogenizer M110-E/H, product made from Microfluidics Corporation). Let this be D liquid. It was 0.440 micrometer when the particle diameter of the inorganic laminar compound in this D liquid was measured in the same solvent.

[0069][Example 2] A 12-micrometer-thick biaxial-stretching polyethylene terephthalate film (inner surface corona treatment article trade name S pet T4102; made by Toyobo Co., Ltd.) is used as a substrate for D liquid produced in Example 1, It applied and dried and the layered product was obtained so that it might become 0.05 micrometer of dry membrane thickness with the drying temperature of 100 \*\* by line velocity/of 6 m using a micro photogravure coating machine. When dry laminate of the 40-micrometer-thick unextended LLDPE film (inner surface corona treatment article trade name; TUS-FCS#40; made by TOH CELLO CO., LTD.) was carried out to the layered product obtained in this way using commercial adhesives, the layered product with good transparency was obtained from appearance.

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[Translation done.]

## \* NOTICES \*

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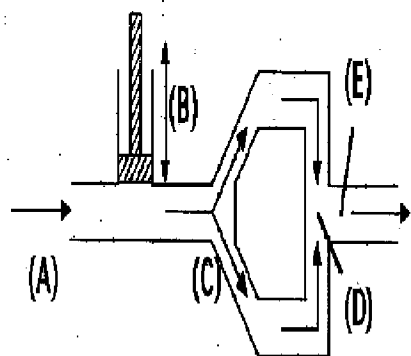
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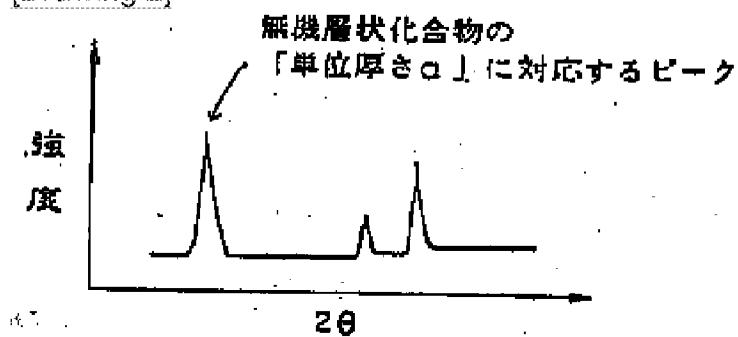
DRAWINGS

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[Drawing 1]

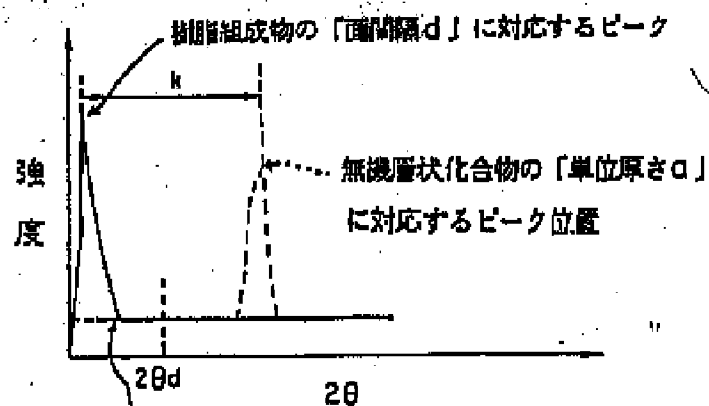


[Drawing 2]



[Drawing 3]



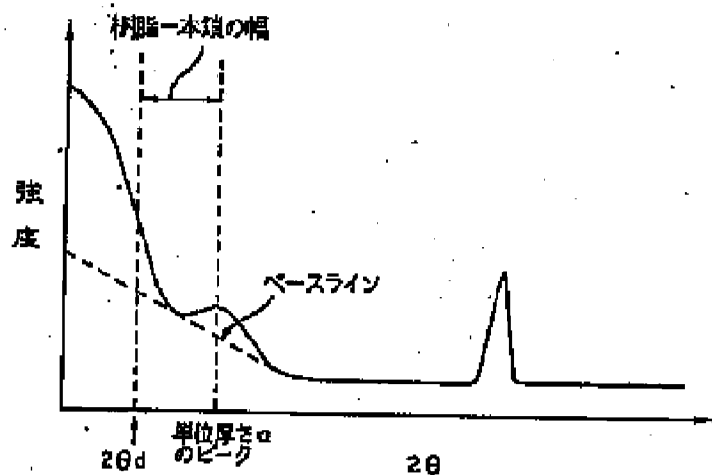


ベースライン

$k$ は長さ換算で樹脂1本鎖の幅以上

$\theta d \rightarrow$ 「単位厚さ $a$  + 樹脂1本鎖の幅」に相当する回折角

[Drawing 4]



[Translation done.]

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## DESCRIPTION OF DRAWINGS

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### [Brief Description of the Drawings]

[Drawing 1]Drawing 1 is a figure showing typically a high pressure dispersion apparatus internal structure and the mechanism of making a detailed state distributing particles by high voltage and high shearing processing.

[Drawing 2]Drawing 2 is a graph which indicates typically a relation with "unit thickness a" of this compound to be an X diffraction peak of an inorganic laminar compound.

[Drawing 3]Drawing 3 is a graph which indicates typically a relation with the "spacing d" of this constituent to be an X diffraction peak of the resin composition containing an inorganic laminar compound.

[Drawing 4]Drawing 4 is a graph which indicates typically a relation with the "spacing d" of this constituent to be an X diffraction peak of a resin composition when it is difficult for the peak corresponding to "the spacing d" to lap with halo (or background), and to detect. In this figure, area of the portion excluding the baseline by the side of a low angle from 2theta is made into the peak corresponding to "the spacing d."

### [Description of Notations]

A: Sample injection

B: Pump application of pressure

C: Channel branching

D: A collision and shear

E: \*\*\*\*\* and processing completion

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[Translation done.]